

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-242249

(43)Date of publication of application : 07.09.2001

(51)Int.Cl.

G01T 1/04
B01J 13/02
C09B 67/08
C09D 7/12
C09D 11/10
C09D201/00
C09K 3/00
C09K 9/02

(21)Application number : 2000-060379

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(22)Date of filing : 01.03.2000

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(54) MICROCAPSULE CONTAINING RADIATION SENSITIVE COMPOSITION AND UTILIZATION METHOD THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide material colored or discolored selectively sensing only radiation (particularly radiation of low dose) while being insensitive to visible light and ultraviolet rays.

SOLUTION: This microcapsule contains a radiation sensitive composition with (a) leuco compound and (b) organic halogen compound as essential components.

LEGAL STATUS

[Date of request for examination] 28.11.2001

[Date of sending the examiner's decision of rejection] 22.06.2004

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

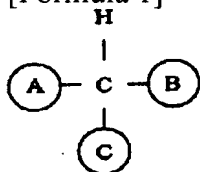
[Claim 1] (a) Leuco compound And microcapsule containing the radiation induction constituent which uses (b) organic halogenated compound as an indispensable component.

[Claim 2] (a) Leuco compound And microcapsule which used (b) organic halogenated compound as the indispensable component, and contained the radiation induction constituent containing the (c) organic solvent and/or the (d) antioxidant further.

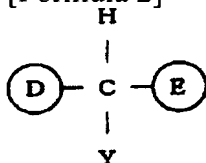
[Claim 3] A leuco compound (a) Triphenylmethane color phthalides and fluoran Phenothiazins, phenazines, indolyl phthalides, and leuco auramine SUPIRO pyrans, SUPIRO free-wheel-plate runs, SUPIRO naphth oxazine, and naphth pyrans Rhodamine lactams, rhodamine lactone, indoline, and diphenylmethanes The microcapsule according to claim 1 or 2 which is chosen from the group which consists of triphenylmethane colors, aza-phthalides, triazene, KUROMENO Indore, xanthenes, diacetylenes, naphth lactams, and azomethines and which is a kind at least.

[Claim 4] (a) The microcapsule according to claim 1, 2, or 3 with which a leuco compound is chosen from the group of the compound shown by the following-izing 1 or ** 2 and which is a kind at least.

[Formula 1]



[Formula 2]



(Among the above-mentioned formula, the aromaticity ring or heterocycle of 5 members which may have the substituent, respectively, or 6 members could be shown, and, as for Rings A, B, C, D, and E, one or more aromaticity rings or heterocycle may condense these, and the bridge may be further constructed over each ring by O, N, or S mutually.) Moreover, Y exists, when main carbon does not conjugate with Rings D and E, and it shows hydrogen, a hydroxy group, an alkoxy group, or an aryloxy group.

[Claim 5] (c) The microcapsule according to claim 1, 2, 3, or 4 which is chosen from the group which an organic solvent becomes from alcohol, ester, and aromatic hydrocarbon and which is a kind at least.

[Claim 6] The microcapsule according to claim 1, 2, 3, 4, or 5 which is what a microcapsule induces a radiation with a 0.001Gy or more level [dosage] of 20000Gy or less, and colors or discolors.

[Claim 7] The radiation induction ink or the coating given in any of claims 1-6 they are which comes to contain a microcapsule.

[Claim 8] The radiation detection approach of detecting the existence of the radiation irradiation to this base by printing or applying ink or a coating according to claim 7 to a base.

[Claim 9] The radiation induction indicator which consists of a base material which contained the microcapsule given in any of claims 1-6 they are at least.

[Claim 10] The radiation induction indicator characterized by forming the radiation induction layer which comes to contain a microcapsule given in any of claims 1-6 they are at least on a base material.

[Claim 11] The radiation induction indicator characterized by forming at least the radiation induction layer which comes to contain a microcapsule, and an ultraviolet absorption layer and/or a visible-ray absorption layer given in any of claims 1-6 they are on a base material.

[Claim 12] The radiation detection approach of detecting the existence of the radiation irradiation to this base by sticking a radiation induction indicator according to claim 9, 10, or 11 on a base.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the radiation induction constituent content microcapsule which can be used suitably, and the various methods of using the microcapsule in the industrial field which needs to detect a radiation.

[0002]

[Description of the Prior Art] The attempt which is going to detect a radiation has been made for many years using the various compounds which induce a radiation, and are colored or discolored. For example, the thing using the constituent which consists of the leuco compound and radical generating agent of specific structure etc. is known as such an attempt (JP,49-28449,B).

[0003] However, although it had the property in which the above-mentioned conventional constituent induced a radiation and colored, the trouble of sympathizing with various exposure lines other than a radiation, for example, a visible ray, ultraviolet rays, etc., and coloring similarly consisted.

[0004] Therefore, only by checking the coloring condition, it could not judge immediately whether it was coloring by the radiation sure enough, and was not able to be used at all to that it cannot be used as a detection means of a reliable radiation, and an application which is concerned with a human life from the possibility of an exposure occasionally according to the misconception decision.

[0005] then, when it supposes un-responding the above-mentioned constituent to a visible ray or ultraviolet rays (that is, it stabilizes -- making) and was going to make it respond alternatively only to a radiation in order to cancel the above-mentioned trouble, it became what induces only the radiation of a high dose extremely, and the unescapable technical technical problem of it becoming impossible to detect the radiation of a low dose consisted.

[0006] Although there is now a strong request from each industrial world for this reason, it does not respond to a visible ray, ultraviolet rays, etc., and the ingredient which responds alternatively, and is colored or discolored only to a radiation (especially radiation of a low dose) is in the present condition which is not yet known.

[0007]

[Problem(s) to be Solved by the Invention] The place which it is made in view of such the present condition, and is made into the purpose has this invention in offering a means to sweep away an above-mentioned trouble by not responding to a visible ray, ultraviolet rays, etc. and finding out the ingredient which responds alternatively, and is colored or discolored only to a radiation (especially radiation of a low dose).

[0008]

[Means for Solving the Problem] If the specific radiation induction constituent was microencapsulated as a result of repeating examination wholeheartedly, in order to solve the above-mentioned technical problem, when this invention persons will acquire knowledge that it can sympathize neither with a visible ray nor ultraviolet rays but can respond alternatively only to a radiation and will repeat research further based on this knowledge, they come to complete this invention at last.

[0009] That is, this invention has a configuration as follows.

1. (a) leuco compound And microcapsule containing the radiation induction constituent which uses (b) organic halogenated compound as an indispensable component.

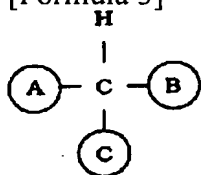
2. (a) leuco compound And microcapsule which used (b) organic halogenated compound as the indispensable component, and contained the radiation induction constituent containing the (c) organic solvent and/or the (d) antioxidant further.

(A) Leuco Compound 3. Triphenylmethane Color Phthalides and Fluoran Phenothiazins, phenazines, indolyl

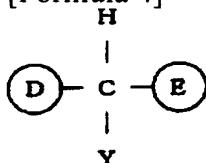
phthalides, and leuco auramine SUPIRO pyrans, SUPIRO free-wheel-plate runs, SUPIRO naphth oxazine, and naphth pyrans Rhodamine lactams, rhodamine lactone, indoline, and diphenylmethanes A microcapsule the above 1 which is chosen from the group which consists of triphenylmethane colors, aza-phthalides, triazene, KUROMENO Indore, xanthenes, diacetylenes, naphth lactams, and azomethines and which is a kind at least, or given in two.

4. Microcapsule of the above 1 and 2 as which (a) leuco compound is chosen from group of compound shown by following-izing 3 or ** 4 and which is kinds at least, or three publications.

[Formula 3]



[Formula 4]



(Among the above-mentioned formula, the aromaticity ring or heterocycle of 5 members which may have the substituent, respectively, or 6 members could be shown, and, as for Rings A, B, C, D, and E, one or more aromaticity rings or heterocycle may condense these, and the bridge may be further constructed over each ring by O, N, or S mutually.) Moreover, Y exists, when main carbon does not conjugate with Rings D and E, and it shows hydrogen, a hydroxy group, an alkoxy group, or an aryloxy group.

5. Microcapsule of the above 1, 2, and 3 which is chosen from group which (c) organic solvent becomes from alcohol, ester, and aromatic hydrocarbon and which is kinds at least, or four publications.

6. Microcapsule the above 1, 2, 3, and 4 which is what microcapsule induces radiation with a 0.001Gy or more level [dosage] of 20000Gy or less, and colors or discolors, or given in five.

7. Radiation induction ink or coating given in any of the above 1-6 they are which comes to contain microcapsule.

8. Radiation detection approach of detecting existence of radiation irradiation to this base by printing or applying ink or coating of seven above-mentioned publication to base.

9. Radiation induction indicator which consists of base material which contained microcapsule given in any of the above 1-6 they are at least.

10. The radiation induction indicator characterized by forming the radiation induction layer which comes to contain a microcapsule given in any of the above 1-6 they are at least on a base material.

11. The radiation induction indicator characterized by forming at least the radiation induction layer which comes to contain a microcapsule, and an ultraviolet absorption layer and/or a visible-ray absorption layer given in any of the above 1-6 they are on a base material.

12. The radiation detection approach of detecting the existence of the radiation irradiation to this base by sticking a radiation induction indicator the above 9 and 10 or given in 11 on a base.

[0010] This invention is the (a) leuco compound. And although it is a photosensitive thing and sympathizes with any exposure line in itself [radiation induction constituent] which consists of a (b) organic halogenated compound, if this is microencapsulated, it will be made based on discovery of the surprising new fact of becoming what responds alternatively only to a radiation and becoming non-sensitivity to exposure lines, such as a visible ray and ultraviolet rays.

[0011] As above-mentioned, the greatest description of this invention is in the point of having connoted the radiation induction constituent of a specific presentation in the microcapsule, and is that should respond alternatively only to the radiation and it presupposed un-responding this constituent (stabilization) to exposure lines other than radiations, such as a visible ray and ultraviolet rays, by this microencapsulation.

[0012] Why this invention shows such alternative effectiveness cannot yet be solved about that detailed mechanism, although guessed because this constituent is probably stabilized by operation of this special system to a visible ray etc. by enclosing the above-mentioned constituent with the minute independent closed system of a microcapsule.

[0013] However, it is thought that the above alternative effectiveness of this invention is based anyway on the new and characteristic operation effectiveness in accordance with the microencapsulation which is not known at all until now.

[0014] When this invention has such a description, in the point that the ingredient which responds alternatively, and is colored or discolored to the radiation of a low dose of 0.001Gy or more 20000Gy or less especially made conventionally impossible could be offered, the availability on the industry is very big.

[0015] Hereafter, it explains per this invention and also to a detail. The radiation selection induction microcapsule of this invention is the (a) leuco compound. And the radiation induction constituent which used (b) organic halogenated compound as the indispensable component, or the radiation induction constituent which contains the (c) organic solvent and/or the (d) antioxidant further is microencapsulated. Then, each above-mentioned requirement for a configuration of this invention etc. is explained in full detail below.

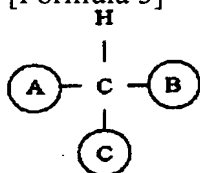
[0016] (1) Anything can use especially various kinds of leuco coloring matter conventionally known as a leuco compound leuco compound as well-known back-coated paper / coloring matter for thermographic papers, and the various leuco coloring matter which are known by the list as various coloring matter precursors in addition to this without limitation.

[0017] When the example is given, for example Triphenylmethane color phthalides and fluoran Phenothiazins, phenazines, indolyl phthalides, and leuco auramine SUPIRO pyrans, SUPIRO free-wheel-plate runs, SUPIRO naphth oxazine, and naphth pyrans Although rhodamine lactams, rhodamine lactone, indoline, diphenylmethanes, triphenylmethane colors, aza-phthalides, triazene, KUROMENO Indore, xanthenes, diacetylenes, naphth lactams, and azomethines can be mentioned They are not these things limited to seeing.

[0018] However, in this invention, although illustrated above, it is suitable to adopt diphenylmethanes and the family analogue of those as the triphenylmethane colors especially expressed with the following-izing 5 or ** 6 and the family analogue of those, and a list especially.

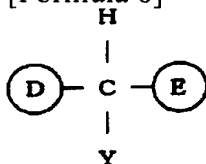
[0019]

[Formula 5]



[0020]

[Formula 6]



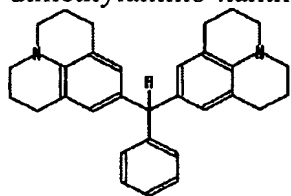
[0021] (Among the above-mentioned formula, the aromaticity ring or heterocycle of 5 members which may have the substituent, respectively, or 6 members could be shown, and, as for Rings A, B, C, D, and E, one or more aromaticity rings or heterocycle may condense these, and the bridge may be further constructed over each ring by O, N, or S mutually.) Moreover, Y exists, when main carbon does not conjugate with Rings D and E, and it shows hydrogen, a hydroxy group, an alkoxy group, or an aryloxy group.

[0022] Here, as an example of the substituent which the above-mentioned rings A, B, C, D, and E may have, although the amino group, a dialkylamino radical, the diaryl amino group, an alkoxy group, an aryloxy group, an acyl group, an acyloxy radical, an alkoxy carbonyl group, an aryloxy carbonyl group, an alkyl group, an aryl group, a hydroxy group, etc. can be mentioned, they are not these things limited to seeing.

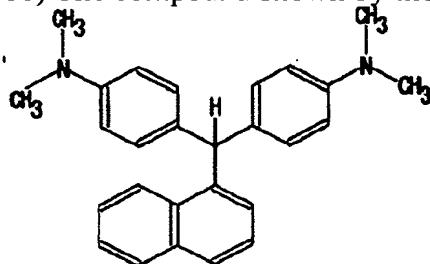
[0023] If the example of the compound shown by the above-izing 5 or ** 6 is given, the following can be mentioned, for example.

[0024] 1) Tris [4- Phenyl] methane 2 tris [4- (Dimethylamino) Phenyl] methane 3 tris [4- (Diethylamino) (Diethylamino) Screw [4-(dimethylamino) phenyl] phenylmethane 5 screw [4-(dimethylamino) phenyl] 4-methoxy phenylmethane 6 -2-methyl-phenyl] methane 4 bis[4-(diethylamino) phenyl] phenylmethane 7 The compound shown by the 9-diethylamino-12-(2-methoxycarbonyl phenyl)-(benzoa) xanthene 82, 8-

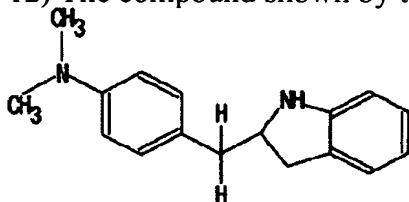
dimethylamino-xanthene 94, and 4'-bis(diethylamino) benzhydrol 10 following-ization 7 [** 7]



11) The compound shown by the following-ization 8 [** 8]



12) The compound shown by the following-ization 9 [** 9]



[0025] (2) Although each well-known thing can be used in principle conventionally and it is not especially limited as an organic halogenated compound organic halogenated compound, it is desirable to use the organic halogenated compound of the structure which is especially easy to emit a halogen radical.

[0026] When an example of such a compound is given, a carbon tetrachloride, tetrabromo methane, Chloroform, bromoform, dichloromethane, dibromomethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, 1,2,3-trichloropropane, 1, 2, 3-TORIBUROMO propane, 1,1,1-trichloroethane, 1, 3-dibromo butane, 1,4-dibromobutane, 1,2-dichloroethane, n-octyl chloride, an isopropyl bromide, a perchloroethylene, trichlene, 1, 2, 3, 4-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,4-trichlorobenzene, o-dichlorobenzene, o-dibromo benzene, P-dichlorobenzene, p-dibromo benzene, monochlorobenzene, A mono-bromobenzene, a mono-iodobenzene, a trichloroacetic acid, alpha-bromoisobutyric acid ethyl ester, Phenyl trifluoromethane, 1 and 1, 3-trihydro tetrafluoro propanol, 4 and 4'-dichloro diphenyl -2, 2-propane, o-chloroaniline, p-chloroacetophenone, o-chlorobenzoic acid, 3,4-dichlorotoluene, o-chloronitrobenzene, p-chlorobenzo trichloride, benzotrifluoride, 3,3'-dichloro-4,4'-diaminodiphenylmethane, N-bromosuccinimide, Although the alpha, alpha, and alpha-tribromonethyl phenylsulfone, 2', and 2'-screw (2-chlorophenyl) -4, 4', 5, and 5'-tetra-phenyl -1, a 1'-BI-1H-imidazole, etc. can be mentioned, it is not limited to these.

[0027] As mentioned above, fundamentally, although the radiation induction constituent of this invention is constituted as an indispensable component, (above-mentioned a) and (b)2 above-mentioned component Usually, although the (b) component is used in the range of 0.01 - 100000 weight section extent to the (a) component 1 weight section and these 2 component is constituted as a uniform compatible condition The class of (a) and (b) both the components to be used and its loadings can be chosen as arbitration according to the class and dosage level of a radiation for detection.

[0028] (3) An organic solvent organic solvent is used as what also shows the function in which the sensitivity over the radiation of the radiation induction constituent of ** this invention can be controlled and adjusted while the function as a ** usual solvent is shown.

[0029] Both the functions as a solvent of the above-mentioned ** are used in order to dissolve them, when it is difficult to make both [these] components into a uniform compatible condition like [in case the case where (above-mentioned a) and (b) both above-mentioned components are a solid-state, and the (b) component are gases]. Furthermore, in order to microencapsulate a certain matter, it may be made into conditions for the matter to be in a liquid condition, but it can also use in order to fulfill such conditions.

[0030] Moreover, since the concentration of (a) in the independent closed system in a microcapsule and (b) both components is adjusted by this, even if the control function of the above-mentioned ** is the case where the same (a) and the (b) component are used, it becomes possible to be able to change the induction level to a radiation of it freely.

[0031] Instantiation of the organic solvent in which such a function is shown mentions various kinds of things, such as an alcoholic system, an ester system, a ketone system, an ether system, an acid AMAIDO system, and an aromatic series system. More specifically Ethanol, a butanol, an octanol, lauryl alcohol, Stearyl alcohol, oleyl alcohol, behenyl alcohol, Ethylene glycol, a glycerol, butyl acetate, lauric-acid lauryl, Palmitic-acid Millis Chill, methyl stearate, a dioctyl phthalate, Phthalic acid diisononyl ester, dioctyl adipate, diisodecyl adipate, Phosphoric-acid TORIKURESHIJIRU, an acetone, methyl isobutyl ketone, a cyclohexanone, A distearyl ketone, an acetophenone, a benzophenone, diethylether, The distearyl ether, diethylene glycol monoethyl ether, Cellosolve acetate, a tetrahydrofuran, dioxane, stearin acid AMAIDO, oleic acid AMAIDO, benzene, toluene, a xylene, ethylbenzene, naphthalene, isopropyl naphthalene, etc. can be mentioned. Although it is not these things limited to seeing, it is desirable to use alcohol, ester, aromatic hydrocarbon, etc. especially.

[0032] In this invention, although it is independent [each] or these organic solvents can be used combining two or more sorts of things, the amount used is usually enough, if it uses in the amount of 1 - 100000 weight section extent to the (a) component 1 weight section.

[0033] (4) The radiation selection induction microcapsule of antioxidant this invention It is (a) as mentioned above. And although the radiation induction constituent which used the (b) component as the indispensable component, or the radiation induction constituent which contains the (c) component further is microencapsulated and sensitivity is alternatively shown only in a radiation The sensitivity over a visible ray, ultraviolet rays, etc. can be further reduced by adding an antioxidant to these constituents.

[0034] In this invention, that such an outstanding description is shown by the antioxidant is the effectiveness found out for the first time by research of this invention person, and it is the new operation effectiveness which was not conventionally known as a function of an antioxidant.

[0035] As such an antioxidant, each well-known antioxidant can be used conventionally, and it is not limited especially.

[0036] When the example is given here, for example 2, 6-G tert-butyl-p-cresol, 2,2'-methylene bis - (4-methyl-6-tert-butylphenol), 4,4'-thiobis - (3-methyl-6-tert-butylphenol), 3, 9-screw [1 and 1-dimethyl-2-[beta-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionyloxy] ethyl] tetraoxaspiro [2, 4, 8, and 10-] [5, 5] undecane, 1, 1, 3-tris-(2-methyl-4-hydroxy-5-tert-buthylphenyl) butane, Tetrakis-[methylene-3-(3' and 5'-G tert-butyl-4'-hydroxyphenyl) propionate] methane, Tocopherols, tocotrienols, dilauryl thiodipropionate, Triphenyl phosphite, tris (nonylphenyl) phosphite, Diisodecyl pentaerythritoldiphosphite, 10-DESHIROKISHI -9, 10-dihydro-9-OKISA-10-phosphaphenanthrene, Although cyclic-neopentane-tetralbis (2, 4-G tert-buthylphenyl) phosphite, 2,2-methylene bis (4, 6-G tert-buthylphenyl) octylphosphite, etc. can be mentioned, they are not these things limited to seeing.

[0037] Such an antioxidant can be used in the amount of 0.0001 - 100 weight section extent to the (a) component 1 weight section.

[0038] (5) As long as the microcapsule of microcapsule this invention can connote the above-mentioned radiation induction constituent as a minute independent closed system fundamentally, the class of the microencapsulation approach or microcapsule wall membrane matter is not limited at all, but no matter it may be what a well-known thing, it can be applied conventionally.

[0039] As the microencapsulation approach, although the coacervation method, interfacial polymerization, an in situ (in situ) polymerization method, hardening-among liquid coating, suspension-among mind coating, a spray drying process, etc. can be mentioned, they are not these things limited to seeing, for example.

[0040] In this invention, the microcapsule of a monolayer with a mean particle diameter of about 0.1-500 micrometers which is independent [each] about these approaches, or connotes the constituent of this invention combining two or more sorts of approaches, or a double layer can be obtained.

[0041] In addition, in this invention, although the vocabulary "endocyst" or "wall membrane" is used for convenience, not only the thing of the structure in which the structure of the microcapsule of this invention endocyst-ized the constituent by such wall membrane but the thing of the solid-solution-like structure where below-mentioned resin and a below-mentioned constituent harmonized completely is contained.

[0042] If the suitable example of the matter which forms the microcapsule wall membrane used here in the above-mentioned all directions method is given The polybasic acid chloride and the multiple-valued amine

for forming the multiple-valued amine for forming polyurea wall membrane, and a carbonyl compound and polyamide wall membrane, The multiple-valued isocyanate and the polyhydroxy compound for forming polyurethane wall membrane, The polybasic acid chloride and the polyhydroxy compound for forming polyester wall membrane, The melamine formalin prepolymer for forming the epoxy compound for forming epoxy resin wall membrane, a multiple-valued amine, and melamine resin wall membrane, The urea and formalin prepolymer for forming urea-resin wall membrane, other gelatin, ethyl cellulose, polyvinyl alcohol, a carboxymethyl cellulose, polystyrene, polyvinyl acetate, etc. can be mentioned.

[0043] Moreover, the microcapsule of this invention can also contain an ultraviolet ray absorbent, a color, a pigment, and other various well-known additives by request besides each above-mentioned component.

[0044] (6) Especially the classification of a radiation that detection device this invention makes applicable to detection is not limited, but alpha rays, beta rays, a gamma ray, and an X-ray are begun, and let various kinds of wide range things variously emitted in connection with the heteroatom fission, nuclear reaction, etc., such as an electron ray and a corpuscular ray, be objects.

[0045] Not responding to exposure lines other than radiations, such as a visible ray and ultraviolet rays, as above-mentioned, the microcapsule of this invention responds alternatively only to a radiation, and thereby, although it has the epoch-making mechanism of action of coloring or discoloring, it has the following detection properties.

[0046] ** The microcapsule of this invention usually has the hue of colorlessness or light color, before a radiation is irradiated, but since the hue will change to a dark color if a radiation is irradiated by this, it can perform easily the check of the existence of radiation irradiation, i.e., the detection, by observing such coupling or a discoloration phenomenon.

[0047] ** Since such coloring or a discoloration phenomenon is irreversible, even if it does not observe the middle of the phenomenon on a target in detail, it does not become unknown [the hysteresis of the existence of radiation irradiation].

[0048] ** Since coloring or the discoloration phenomenon of this invention responds and is done so also to the radiation of the very low dosage level of 0.001Gy or more 20000Gy or less, the alternative detection of a low-dose radiation conventionally made impossible by this kind of the simple approach is also possible for it.

[0049] ** Since it can be made to be able to be proportional to the level of the irradiated dosage and concentration change can be carried out, the above-mentioned coloring or a discoloration phenomenon can detect not only the existence of the exposure but dosage level by checking the coloring concentration and discoloration concentration.

[0050] (7) Although an example is hereafter given and explained about the usage of usage this invention, the range of this invention is not these things limited to seeing.

[0051] ** Usual ink and a usual coating can be made to contain the microcapsule of ink and coating this invention. If this ink and coating are printed or applied on various kinds of bases, the existence of an exposure of the radiation to this base can be detected very easily.

[0052] ** The use as an indicator in which the radiation induction layer which comes to contain the microcapsule of this invention was formed on the indicator base material can be mentioned. Moreover, as such an indicator, the base material which mixed the microcapsule of this invention can also constitute.

[0053] (b) As a base material used for a base material indicator, although sheet-like objects, such as various kinds of papers, plastic film, a fiber knit fabric, a nonwoven fabric, and a metallic foil, can be mentioned, these things [being limited to seeing] do not exist, for example.

[0054] (b) As the formation approach of a radiation induction layer established on the formation approach base material of a radiation induction layer, various kinds of approaches are mentioned and it is not limited especially. For example, although it can carry out by printing or applying ink and the coating containing the microcapsule of this invention of the above-mentioned **, even if approaches other than this are adopted, it does not interfere at all.

[0055] Moreover, although the above-mentioned radiation induction layer can be prepared in the whole surface or the part on a base material by the above-mentioned all directions method, it does not pass over such design-technique on the alternative matter which this contractor performs to arbitration, and, thereby, the range of this invention is not limited.

[0056] Therefore, even if various kinds of displays by common ink and the common coating which do not induce a radiation are prepared on the above-mentioned base material, it does not interfere, and when it is hard to check coloring and discoloration of a radiation induction layer by looking when a substrate is a dark color, and becoming, a substrate concealment layer can also be prepared in the bottom of a radiation

induction layer.

[0057] (c) In addition, by request, an ultraviolet absorption layer and/or a visible-ray absorption layer can also be prepared on a radiation induction layer.

[0058] The above-mentioned absorption layer can form these drugs by laminating beforehand content or the films, i.e., an ultraviolet absorption film and various coloured films, which carried out the coat while being able to form it using ink and the coating containing a well-known ultraviolet ray absorbent and the general dyes and pigments which absorb a visible ray conventionally.

[0059] Moreover, such a radiation indicator can also be considered as the configuration in which the protective layer was formed on the front face, in order to protect each formative layer from various external factors effectively.

[0060] ** The microcapsule of this invention for use can be used as a means to perform exposure management very easily, in a nuclear power plant, or the medicine and the research facility which deal with a radiation, the radioactive substance, etc. in addition to this. Moreover, in the facility which performs sterilization and various kinds of processings with a radiation, it can use as a means to detect the quantity of radiation of a radiation easily.

[0061] As such an example of application, the mode used as a check means of whether radappertization processing is performed to agricultural products and the blood for transfusion, such as meat, grain, and fruit, can be mentioned, for example.

[0062]

[Embodiment of the Invention] Although an example is given and this invention is hereafter explained further to a detail, this inventions are not these things limited to seeing. In addition, especially, that it is with the "section" or "%" in the following publications means the "weight section" or "% of the weight", as long as there is no notice.

[0063] "The manufacturing method of a microcapsule"

[Example A of manufacture] Weighing capacity of the radiation induction constituent 25 section of Table 3 is carried out, and this and the epoxy resin [5 by the trade name:Epicoat 828 and oil-ized shell epoxy company] section are mixed to the bottom homogeneity of heating. This mixture is added under churning in the 70-degree C 10% gelatin water-solution 200 section, and emulsification distribution is carried out at the shape of an oil droplet with a diameter of about 10 micrometers. And continuing churning, the curing agent [4 by the trade name:epicure U and oil-ized shell epoxy company] for epoxy resins section is added, solution temperature is raised to 90 degrees C, and it is made to react at the temperature for 4 hours. Then, the microcapsule of this invention containing a radiation induction constituent was obtained by making solution temperature cool to near a room temperature, rinsing the generated granular object and seasoning naturally the back according to **.

[0064] [Example B of manufacture] It adds under churning in the 40-degree C 10% gelatin water-solution 50 section, and the shape of an oil droplet with a diameter of about 20 micrometers is made to carry out emulsification distribution of the radiation induction constituent 10 section of Table 3. Then, these dispersion liquid are added under churning in the 40-degree C 5% gum arabic water-solution 100 section, and pH is adjusted to 4 by dropping an acetic-acid water solution 10%, continuing churning as it is. Then, the formalin 2 section is added in the place which adds slowly 40-degree C warm water the about 100 sections, and it finished adding. Then, after continuing churning for 40 minutes, keeping solution temperature at 40 degrees C, solution temperature is cooled until it becomes 5 degrees C or less, and churning is continued at the temperature of 5 degrees C or less for further 1 hour. Then, after adjusting pH to 9 by dropping a caustic-alkali-of-sodium water solution 10%, solution temperature is raised to 50 degrees C with the programming rate of 1 degree C per minute. The microcapsule of this invention containing a radiation induction constituent was obtained by taking out a granular object and drying a filtration object after rinsing by leaving these dispersion liquid one whole day and night, and carrying out a decantation.

[0065] It adds under churning in the 80-degree C 1% sodium-polyacrylate water-solution 100 section, and the shape of an oil droplet with a diameter of about 5 micrometers is made to carry out emulsification distribution of the radiation induction constituent 10 section of the [example C of manufacture] table 3. Then, the melamine formalin prepolymer 5 section is added in these dispersion liquid, dilute hydrochloric acid is dropped, pH of a system is adjusted to 4.5, continuing churning, and churning is continued at the temperature of 80 more degrees C for 2 hours. Then, the radiation induction constituent content microcapsule which has a sodium-polyacrylate layer on a front face and which consists of melamine resin was obtained by carrying out spray drying of these dispersion liquid with a spray dryer.

[0066]

[Examples 1-64] The example of this invention is given to Tables 1 and 2. The alphabet notation which "No." currently mentioned to above-mentioned front Naka and the column of a "radiation induction constituent" shows "No." of the radiation induction constituent mentioned to Table 3, and is mentioned to the column of a "microcapsule" shall show the alphabet notation of the example of manufacture of the above-mentioned microcapsule. For example, an example 1 shows the microcapsule which microencapsulated radiation induction constituent No.1 of Table 3 by the approach of the example A of microcapsule manufacture.

[0067] Moreover, the hue currently mentioned to the column of "the mode of coloring thru/or discoloration" shows the change at the time of irradiating a 1000Gy gamma ray. For example, an example 1 shows that what was "colorlessness" became "blue" after gamma irradiation before gamma irradiation.

[0068] In addition, the radiation induction constituent indicated to Table 3 mixes each component, and consists of rates of indicated weight number of copies as a uniform compatible condition. It is made to dissolve by warming as occasion demands about what cannot be in a uniform compatible condition easily in a room temperature.

[0069] Moreover, the cable address in Table 3 means the following.

a1 -- Tris [4-(dimethylamino) phenyl] methane (alias name leuco crystal violet)

a2 -- 9-diethylamino-12- (2-methoxycarbonyl phenyl)-benzo (a) Xanthene a3 -- Screw [4- (Diethylamino) Phenyl] phenylmethane a4 -- 4 and 4'-bis(diethylamino) benzhydrol a5 -- 4 and 4'-bis(diethylamino)

benzophenone a6 -- 6-(dimethylamino)-3, 3-screw [4-(dimethylamino) phenyl]-1 (3H)-iso benzohula non a7 -- 2- (2-chloroanilino)-7-dibutylamino-10- (2-methoxycarbonyl phenyl)-xanthene a8 -- 3, 7-dimethoxy [-- delta-tocopherol d3 / -- Dilauryl thiodipropionate [0070]] -10 -(2-ethoxycarbonyl phenyl)- Xanthene d1 -- 2,2'-methylene bis - (4-methyl-6-tert-butylphenol) d2

[Example 65] The radiation induction layer was formed in the shape of an alphabetic character on the white plate using the water paint which consists of the microcapsule 30 section of an example 1, the ethylene-vinyl acetate copolymerization resin emulsion (40% of solid content) 40 section, the silicon system defoaming agent 1 section, the epoxy cross-linking agent 1 section, and the water 28 section by carrying out spray painting to the shape of an alphabetic character of "DANGER." Even if it left the above-mentioned white plate to the outdoors on the 1st, there was no change of a color, but when the 500Gy 60Co(es)-gamma ray was irradiated at this, the alphabetic character blue "DANGER" was clearly formed on this white plate. Consequently, it turned out that the thing of an example can detect the exposure of a gamma ray.

[0071]

[Comparative Example(s)] Except for replacing with the microcapsule 30 section of the above-mentioned example 1, and using the constituent (namely, constituent of No.1 of Table 3 itself) 30 section which is not microencapsulated, all others prepared the water paint like the above, and formed like the above the alphabetic character "DANGER" on the white plate using this coating. And even if the alphabetic character "DANGER" already blue before irradiating a gamma ray by being influenced of the ultraviolet rays included in sunlight when the above-mentioned white plate was left to the outdoors like the above-mentioned example on the 1st is formed and it has already irradiated the 500Gy 60Co(es)-gamma ray at this, the blue hue hardly changed. Consequently, in the thing of the example of a comparison, it turned out that a gamma ray is undetectable.

[0072] If an above-mentioned example 65 and the above-mentioned example of a comparison are compared, it can understand well that the alternative sensitivity over a radiation was given by the microencapsulation means of this invention.

[0073]

[Example 66] The radiation induction indicator of this invention was created according to drawing 1 . the alphabetic character shown by one in drawing carries out printing formation with usual green printing ink on the white PET film A -- having -- **** -- said -- printing formation of the alphabetic character shown by 2 is carried out with usual black printing ink. moreover -- said -- if the area of 3 is white and it applies to area 4-7, it is colored by blue printing ink so that blue concentration may become deep one by one. and -- said -- the printing ink containing the microcapsule of an example 55 is applied to the area of 8. Moreover, although illustration is not carried out, as the whole surface of the indicator concerned is covered, the ultraviolet absorption film laminates, and, on the other hand, the adhesive layer is prepared in the rear face of the indicator concerned.

[0074] The radiation induction indicator of this invention which has the above configuration The radiation induction layer slack area 8 is designed so that blue coloring concentration may differ according to the dosage level of a radiation. One side and area 4-7 (which are colored in such specifically deep blue that

dosage level becomes high) It enables it to detect simply the dose irradiated by comparing the coloring concentration of area 8 with the color of area 4-7 by being classified by color so that it may become equal to the blue concentration according to each dosage level of area 8. (In the case of drawing 1 $R > 1$, area 8 induces the radiation of the dosage level of profile 0.1kGy(= 100Gy) -2kGy (= 2000Gy), and is colored blue.)

[0075] And desired radappertization was able to distinguish very easily whether it carried out on desired dosage level by sticking the indicator concerned on the pack of the blood for transfusion, a medical device, the pack for over-the-counter sales of meat, grain, and fruit through the adhesive layer.

[0076]

[Table 1]

実施例	放射線感受性組成物	マイクロカプセル	発色乃至変色の濃度
1	No. 1	A	無色→青色
2	No. 1	B	無色→青色
3	No. 1	C	無色→青色
4	No. 2	A	無色→青色
5	No. 2	B	無色→青色
6	No. 2	C	無色→青色
7	No. 3	A	無色→青色
8	No. 3	B	無色→青色
9	No. 3	C	無色→青色
10	No. 4	A	無色→青色
11	No. 4	B	無色→青色
12	No. 4	C	無色→青色
13	No. 5	A	無色→青色
14	No. 5	B	無色→青色
15	No. 6	C	無色→青色
16	No. 6	A	無色→青色
17	No. 7	C	無色→青色
18	No. 8	B	無色→青色
19	No. 9	C	無色→青色
20	No. 10	B	無色→青色
21	No. 11	A	無色→青色
22	No. 11	B	無色→青色
23	No. 11	C	無色→青色
24	No. 12	C	無色→青色
25	No. 13	C	無色→青色
26	No. 14	A	無色→青色
27	No. 14	B	無色→青色
28	No. 15	A	無色→青色
29	No. 15	B	無色→青色
30	No. 15	C	無色→青色
31	No. 16	B	無色→青色
32	No. 17	C	無色→青色

[0077]

[Table 2]

実施例	放射線感応 組成物	マイクロ カプセル	発色乃至 脱色の種類
33	No. 18	A	無色→青色
34	No. 18	B	無色→青色
35	No. 18	C	無色→青色
36	No. 19	B	無色→青色
37	No. 20	A	淡黄色→青緑色
38	No. 20	B	淡黄色→青緑色
39	No. 20	C	淡黄色→青緑色
40	No. 21	C	淡黄色→青緑色
41	No. 22	A	無色→青色
42	No. 22	B	無色→青色
43	No. 22	C	無色→青色
44	No. 23	C	無色→青色
45	No. 24	C	無色→青色
46	No. 25	A	無色→青色
47	No. 25	A	無色→青色
48	No. 26	B	無色→青色
49	No. 26	C	無色→青色
50	No. 27	A	無色→青色
51	No. 27	B	無色→青色
52	No. 27	C	無色→青色
53	No. 28	A	無色→青色
54	No. 29	B	無色→青色
55	No. 30	C	無色→青色
56	No. 31	A	無色→青色
57	No. 32	A	無色→青色
58	No. 32	B	無色→青色
59	No. 32	C	無色→青色
60	No. 33	B	無色→赤色
61	No. 34	B	無色→緑色
62	No. 35	C	無色→青色
63	No. 36	A	無色→黒色
64	No. 37	A	無色→黄色

[0078]

[Table 3]

No.	(a) 化合物	(b) 有機ヘロゲン化合物	(c) 有機配剤	(d) 脱色防止剤
1	(100)	モノプロペン (100部)	—	—
2	(100)	ジプロペン (300部)	—	—
3	(100)	トリプロペン (1000部)	—	—
4	(100)	四プロペン (1000部)	—	—
5	(100)	1,1,1,3-テトラプロペン (800部)	—	—
6	(100)	四プロペン (400部)	—	—
7	(100)	1,2,3,4-テトラプロペン (50部)	1-オクタノール (1000部)	—
8	(100)	1,2,3,4-テトラプロペン (50部)	キシレン (1000部)	—
9	(100)	2,2,3,4-テトラプロペン (50部)	ジエチルアジレート (1000部)	—
10	(100)	2,2,3,4-テトラプロペン (50部)	メタン (1000部)	—
11	(100)	モノプロペン (100部)	—	—
12	(100)	キシレン (100部)	—	—
13	(100)	1,2,3,4-テトラプロペン (50部)	—	—
14	(100)	2,2,3,4-テトラプロペン (50部)	1-オクタノール (500部)	—
15	(100)	モノプロペン (100部)	キシレン (1000部)	—
16	(100)	トリプロペン (300部)	—	—
17	(100)	四プロペン (80部)	キシレン (1000部)	—
18	(100)	モノプロペン (100部)	—	—
19	(100)	トリプロペン (500部)	—	—
20	(100)	モノプロペン (100部)	—	—
21	(100)	1,2,3,4-テトラプロペン (500部)	—	—
22	(100)	モノプロペン (100部)	—	—
23	(100)	2,2,3,4-テトラプロペン (50部)	1-オクタノール (1000部)	—
24	(100)	モノプロペン (100部)	—	—
25	(100)	モノプロペン (100部)	キシレン (100部)	—
26	(100)	モノプロペン (100部)	—	di. (0.5部)
27	(100)	モノプロペン (100部)	キシレン (100部)	di. (0.5部)
28	(100)	モノプロペン (100部)	—	di. (1部)
29	(100)	モノプロペン (100部)	—	di. (10部)
30	(100)	モノプロペン (100部)	—	di. (0.5部)
31	(100)	モノプロペン (100部)	—	di. (0.5部)
32	(100)	2,2,3,4-テトラプロペン (50部)	メタン (2000部)	di. (1部)
33	(100)	1,2,3,4-テトラプロペン (1000部)	—	di. (1部)
34	(100)	四プロペン (50部)	キシレン (1000部)	di. (1部)
35	(100)	モノプロペン (100部)	—	di. (1部)
36	(100)	モノプロペン (100部)	—	—
37	(100)	モノプロペン (100部)	—	—

[0079]

[Effect of the Invention] (1) Not responding to exposure lines other than radiations, such as a visible ray and ultraviolet rays, the microcapsule of this invention responds alternatively only to a radiation, and, thereby, has the epoch-making operation effectiveness of coloring or discoloring.

[0080] (2) Even if coloring or the discoloration phenomenon of this invention is irreversible and does not observe the middle of the phenomenon on a target in detail, it does not become unknown [the hysteresis of the existence of radiation irradiation].

[0081] (3) Since such coloring or a discoloration phenomenon responds also to the radiation of the very low

dosage level of 0.001 Gy or more 20000 Gy or less and it is done so, the utility value on the point which enabled conventionally alternative detection of a low-dose radiation made impossible by this kind of the simple approach, and its industry is very big.

[0082] (4) Since it can be made to be able to be proportional to the level of the irradiated dosage and concentration change can be carried out, the above-mentioned coloring or a discoloration phenomenon is advantageous by checking the coloring concentration and discoloration concentration at the point that not only the existence of the exposure but dosage level is detectable.

[Translation done.]

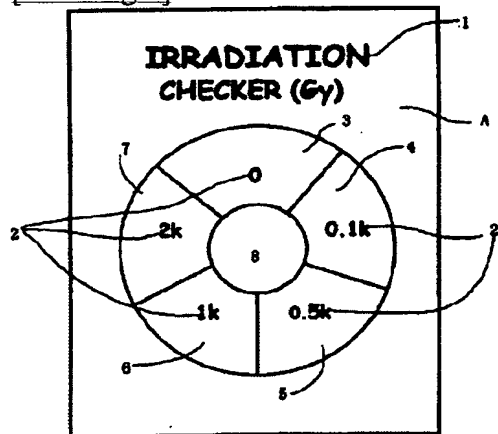
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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Translation done.]